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Some of the most efficient methods for studying systems having a large number of degrees of freedom treat a few degrees of freedom quantum mechanically and the remainder classically. Here we examine how these methods fare when used to calculate the cross section for photon absorption by a quantum system imbedded in a medium. To test the method we study a model which has two degrees of freedom and mimics the properties of an one dimensional alkali atom - He dimer. We treat the electron motion quantum mechanically and distance between the He atom and the alkali ion classically. Light absorption occurs because the electron is coupled to radiation. The calculation of the absorption cross section by quantum-classical methods fails rather dramatically: at certain frequencies the absorption coefficient is negative. By comparing with exact quantum calculations we show that this failure takes place because the time evolution of the classical variables influences the dynamics of the quantum degree of freedom through the Hamiltonian only; important information, which a fully quantum treatment would put in the wave function, is missing. To repair this flaw we experiment with a method which uses a swarm of classical trajectories to generate a "classical wave function". The results are encouraging but require substantial computer time when the number of classical variables is large. We argue that in the limit of many classical degrees of freedom accurate calculations can be performed by using the time dependent Hartree method and treating some degrees of freedom by exact numerical methods (e.g. an FFT procedure) and the others by Gaussian wave packets or any other propagation method that is accurate for a very short time. This procedure leads to a simple time domain picture of dephasing and line broadening in the case of a localized quantum system imbedded in a medium with heavy atoms.

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A test of the possibility of calculating absorption spectra by mixed quantum - classical methods

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A TEST OF THE POSSIBILITY OF CALCULATING ABSORPTION SPECTRA BY MIXED QUANTUM - CLASSICAL METHODS.

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Abstract: Some of the most efficient methods for studying systems having a large number of degrees of freedom treat a few degrees of freedom quantum mechanically and the remainder classically. Here we examine how these methods fare when used to calculate the cross section for photon absorption by a quantum system imbedded in a medium. To test the method we study a model which has two degrees of freedom and mimics the properties of an one dimensional alkali atom - He dimer. We treat the electron motion quantum mechanically and the distance between the He atom and the alkali ion classically. Light absorption occurs because the electron is coupled to radiation. The calculation of the absorption cross section by quantum-classical methods fails rather dramatically: at certain frequencies the absorption coefficient is negative. By comparing with exact quantum calculations we show that this failure takes place because the time evolution of the classical variables influences the dynamics of the quantum degree of freedom through the Hamiltonian only; important information, which a fully quantum treatment would put in the wave function, is missing. To repair this flaw we experiment with a method which uses a swarm of classical trajectories to generate a "classical wave function". The results are encouraging but require substantial computer time when the number of classical variables is large. We argue that in the limit of many classical degrees of freedom accurate calculations can be performed by using the time dependent Hartree method and treating some degrees of freedom by exact numerical methods (e.g. an FFT procedure) and the others by Gaussian wave packets or any other propagation method that is accurate for a very short time. This procedure leads to a simple time domain picture of dephasing and line broadening in the case of a localized quantum system imbedded in a medium with heavy atoms.

I. Introduction

Calculations in which several degrees of freedom are treated quantum mechanically and the remainder classically are very popular[1]. All such algorithms divide the degrees of freedom in two classes denoted here symbolically by q and c. The dynamics of the q-degrees of freedom is determined by solving the time dependent Schrödinger equation

$$i\hbar\partial\psi(q;t)/\partial t = [K + V(q,c(t))]\,\psi(q;t). \qquad (I.1)$$

The kinetic energy operator K depends only on the coordinates q. The classical coordinates in the potential energy are replaced by their classical values c(t) at time t. The latter satisfy the classical equation of motion

$$m\,d^2c(t)/dt^2 = -\partial\left\{\int dq\,\psi(q;t)^*\,V(q,c(t))\,\psi(q;t)\right\}/\partial c(t), \qquad (I.2)$$

where the interaction energy is averaged over the quantum degrees of freedom. Other choices for the classical equation of motion are possible; the one given above is the most popular. In what follows we call any method described by algorithms based on (I.1-2) a traditional quantum - classical method (TQC). The name quantum-classical method (QC) is reserved for a method proposed here which uses classical trajectories to construct a wave function for the c-degrees of freedom.

In this algorithm the properties of the classical degrees of freedom are not described by a wave function. They influence quantum dynamics as time

dependent parameters in Eq. (I.1).

Because of the large number of applications to a great variety of problems it is not possible to make a broad statement regarding the accuracy of this procedure. Wahnstrom *et al* [1c] have used it to calculate the correlation functions appearing in the theory of the rate constant. They found that the results given by the quantum-classical (TQC) method were very close to the fully quantum ones, as long as the mass of the classical degrees of freedom was sufficiently large. Alimi *et al.*[1d] compared the dynamics of a wave packet (describing the quantum degree of freedom) coupled to a classical particle, to the exact quantum behavior of the same system and were satisfied with the results. Both studies were interested in short time dynamics of systems for which the wave function describing the q-degree of freedom did not split into spatially separated pieces. These conditions favor the TQC method[2].

In discussing the results of the TQC method we found it useful to distinguish two kinds of quantities: observables that have a classical interpretation, which have the form

$$\langle \psi,t | O | \psi,t \rangle, \tag{I.3}$$

where $|\psi,t\rangle$ is the wave function at time t and O is an operator representing a physical quantity; and quantities that do not have a classical analog, which have the form

$$\langle \psi,t | O | \psi,0 \rangle, \tag{I.4}$$

where $|\psi,0\rangle$ is the wave function at time zero.

All the examples which have shown that the TQC method works well have calculated observables that have a classical interpretation. In this article we examine whether the same is true when non-classical quantities having the form (I.4) are computed. The calculation of the cw absorption and Raman cross section by time domain methods (i.e which use Heller's[3] formulae) provide important examples of such quantities. There are very few examples of the computation of an absorption cross section by TQC methods. Gerber and Alimi[1c] have reported in passing one calculation of an overlap integral between and initial wave function and its value at time t. In our opinion the results were fairly poor even at early times when the method is expected to perform best. Another such calculation was performed by Thirumalai, Bruskin and Berne[1d] who calculated the absorption spectrum of Br_2 in an Ar matrix. They treated Ar motion classically and the Br_2 bond length by Heller's Gaussian Wave Packets (GWP) method. These authors were mostly interested in the adequacy of the GWP for describing the quantum degree of freedom and not in testing the quantum-classical procedure.

Our study is carried out by performing numerical experiments on a two dimensional model for which the absorption cross section can be computed fully quantum mechanically by numerical methods. The accuracy of the TQC method is then determined by comparing its results to those of the exact quantum calculations. The TQC results are extremely poor: the absorption spectrum (i.e. the absorption rate) is negative at some frequencies.

The model has not been devised to give the TQC method trouble. It consists of an ionic core, an electron and a He atom interacting through reasonable potentials. The position of the electron is treated quantum mechanically and that of the He-ion distance classically. The electron is coupled to the electric field of the laser and absorbs light; the He atom influences this process only through its action on the electron. One can think of this as an one dimensional model for a Na atom weakly bound to a He atom. Since the electron is the main actor in the absorption process and He has a supporting role, one would expect that not much is lost if He is treated classically. The mass disparity between the two particles is large and the time in which the electron samples its environment to build the structure in the spectrum is extremely short. Both conditions increase the chance that a quantum- classical treatment will give reasonable results.

The negative absorption rate is not an accidental property of our model. It is also present if we change the potentials to mimic the system HIHe for which the TQC method gives good results for quantities that have a classical analog[1d]. The failure is not caused by the low dimensionality of the model: the absorption cross sections of I_2 Xe_{10} or $e^-Na^+Xe_{10}$ has the same unpleasant feature[4].

By experimenting with the model we found that the negative rate appears because the TQC method approximates the total wave function $\Psi(q,c;t)$ with

$$\Psi(q,c;t) \approx \psi(q;t). \qquad (I.5)$$

This contains no information regarding the c-degrees of freedom. The latter

affect absorption only because their classical motion modulates the potential energy in the Eq. (I.1) describing the time evolution of $\psi(q;t)$. To avoid this oversimplification we use

$$\Psi(q,c;t) \approx \psi(q;t)\, A(c;t) \exp(i\, S(c;t)/\hbar), \qquad (I.6)$$

Here A(c;t) and S(c;t) are real functions of the positions of the classical particles. A and S are calculated by propagating a swarm of classical trajectories whose initial conditions mimic the initial quantum state of the c-degree of freedom. The square root of the density of these trajectories in the neighborhood of the point c at time t gives A(c;t); S(c;t) is the sum of the principal Hamilton functions for the trajectories that have reached the neighborhood of c at time t. The absorption spectrum calculated from the wave function $\Psi(q,c;t)$ defined by the above procedure is close to that obtained by the exact quantum calculations. The accuracy deteriorates for long time calculations and therefore the method is not useful if one is interested in low resolution spectra. In the case that the system is imbedded in a condensed medium this is not a handicap; the spectra of such systems are broad and thus are not altered by low resolution measurements.

This calculation requires about the same amount of computer time as the traditional TQC method. The method can be used to calculate Raman spectra, electronic absorption spectra and to solve curve crossing problems. Since we have not derived validity criteria for this approximation it is not prudent to use it in new applications without testing it on simplified models for which exact calculations are possible.

The reasons for the failure of the TQC method are then examined in the

context of Heller's[3a] time dependent description of the absorption spectrum. As was explicitly pointed out by Heller[3c] and by Messina and Coalson[4] all the degrees of freedom in a complex system affect the absorption line shape. In the present case the medium's degrees of freedom influence the absorption spectrum because overlap of their wave function at a time t with the initial wave function decays with t[3a] on a time scale which gives the spectrum its width. The TQC method erroneously assumes this decaying overlap to be equal to one. The calculations reported here show that the error cause by this replacement is dramatic and of a qualitative nature.

A detailed analysis (Section VII) suggests that when the excitation of the absorber affects *a large number* of the degrees of freedom in the medium, the absorption cross section can be accurately calculated by using short time quantum methods to describe the dynamics of the medium's degrees of freedom. This is extremely efficient computationally. Unfortunately it works only for a large number of classical degrees of freedom and therefore its accuracy cannot be tested by comparison with fully quantal numerical results.

II. The Models

To test various TQC procedures we calculate the absorption spectrum of a colinear system consisting of an electron (located at r), an ion of infinite mass (located at the origin) and an atom having the mass of He (located at R). The interaction energies are physically reasonable but do not represent accurately the alkali -He system. Nevertheless, we will use the names alkali atom (or ion) and He for the particles defining the system.

The alkali ion - electron interaction energy V_{ei} is

$$V_{ei}(r) = -e^2/r_c \qquad \text{if} \quad r < r_c$$
$$V_{ei}(r) = -e^2/r \qquad \text{if} \quad r_c < r. \qquad \text{(II.1)}$$

e is the electron charge and r_c is a cutoff parameter whose value is specified below. Eq.(II.1) was suggested by Shaw[6a] and has been used by Rahman and Parinello[6b] , Selloni,Carnevali,Carr and Parinello[7] , and Haug and Metiu[8].

The electron-helium interaction energy is that used by Coker, Berne and Thirumalai [9] (for electron-xenon)

$$V_{ea}(X) = \sum_n (a/X^4)\,[\,b/(c+X^6) - 1\,], \qquad \text{(II.2)}$$

where

$$X = \min\{|r-R|\,,\, R_c\}, \qquad \text{(II.3)}$$

$a = 26.86$ eV Å^4 , $b = 108.0$ Å^6 , $c = 83.29$ Å^6. The cutoff distance $R_c = 0.5$ Å makes the potential finite (and constant) at short distances. The total electron interaction energy is

$$V_{en}(r,R) = V_{ei}(r) + V_{ea}(r,R). \qquad \text{(II.4)}$$

The alkali ion -helium interaction energy is given by a harmonic potential which roughly approximates the potential well of the potassium ion - xenon interaction[10]

$$V_{ia}(R) = (1/2)M\omega^2R^2 ; \qquad (II.5)$$

R is the atom-ion distance and $\omega = 0.1$ eV.

The momenta associated with the positions (r,R) are denoted by (p,P). The Hamiltonian is

$$H = H_{ia}(R, P) + H_{en}(r,p;R). \qquad (II.6)$$

H_{ia} , describing the ion - atom internuclear motion, is given by

$$H_{ia} = P^2 / (2M) + V_{ia}(R) . \qquad (II.7)$$

The term

$$H_{en} = p^2/(2m) + V_{en}(r,R) \qquad (II.8)$$

contains the kinetic energy of the electron plus its interaction energy with the ion and the rare gas.

III. Exact and time dependent Hartree calculation of the absorption cross section

The absorption cross section $\sigma(\omega)$ for a system initially in the ground state $|\Psi_g\rangle$ is

$$\sigma(\omega) \sim \omega \, \mathrm{Re} \int_0^\infty dt \exp(i\omega t) \; C(t) \; , \tag{III.1}$$

with

$$C(t) = \exp(iE_g t/\hbar) \langle \Psi_p(0) | \Psi_p(t) \rangle . \tag{III.2}$$

$\langle \Psi_p(0) | \Psi_p(t) \rangle$ is the overlap integral between the promoted wave function

$$|\Psi_p\rangle = -r \, |\Psi_g\rangle , \tag{III.3}$$

at time t=0 and the promoted wave function

$$|\Psi_p(t)\rangle = U(t) |\Psi_p\rangle \tag{III.4}$$

at time t. U(t) is the molecular (the field is not included) propagator, E_g is the ground state energy and r is the electron position.

These equations are similar to those proposed by Heller[3a], except for the fact that the transition dipole matrix element in the Heller formula is replaced by the electron position. This modification is necessary because we treat the electron motion explicitly.

The spectra reported here are calculated from

$$\sigma(\omega;\tau) \sim \omega \, \mathrm{Re} \int_0^\infty dt \, f_\tau(t) \exp(i\omega t) \, C(t). \qquad \text{(III.5)}$$

This equation gives a low resolution version of the exact spectrum. The peak width $\Delta\omega \sim 2\pi/\tau$ is set by the time constant τ in the "window" function[11]

$$f_\tau(t) = \exp[-(t/\tau)^2]. \qquad \text{(III.6)}$$

The computation of the ground state and of the promoted state evolution are sketched in Appendix A.

The starting point of all TQC procedures is the assumption that there are no statistical (i.e.quantum) correlations between the q and c variables (i.e. the wave function has the form $\phi(q)\chi(c)$). For the simple system considered here this approximation is identical to the time dependent Hartree (TDH) approximation. To distinguish the errors introduced by neglecting quantum correlations from those caused by using classical dynamics we perform calculations with the TDH method and compare them to the exact ones. In the TDH calculations the ground state and the promoted state have the form

$$\langle r,R \,|\, \Psi_g \rangle \approx \langle r \,|\, \phi_g \rangle \langle R \,|\, \chi_g \rangle \exp(i\eta_g/\hbar). \qquad \text{(III.7)}$$

and

$$\langle r,R|\Psi_p\rangle \simeq \langle r|r|\phi_g\rangle \langle R|\chi_g\rangle \exp(i\eta_g/\hbar) \equiv \langle r|\phi_p\rangle \langle R|\chi_g\rangle \exp(i\eta_g/\hbar) \qquad \text{(III.8)}$$

The phase $\exp(i\eta_g/\hbar)$ - which is called in what follows the Hartree phase - is introduced to simplify the form of the TDH equations of motion.

Substituting the Hartree form (III.8) of the wave function into the Eq.(III.2) for the overlap integral leads to

$$C_h(t) = \exp(iE_g t/\hbar) \langle\phi_p(0)|\phi_p(t)\rangle \langle\chi_g(0)|\chi_g(t)\rangle \exp(i[\eta_g(t)-\eta_g(0)]/\hbar). \qquad \text{(III.9)}$$

The notation $C_h(t)$ indicates that the overlap integral is calculated by using the TDH wave function. The latter are obtained by solving the TDH equations[12].

$$i\hbar \frac{\partial}{\partial t} |\phi_p\rangle = [\, p^2/2m + V_{ei}(r) + \langle\chi_g|V_{ea}(r,R)|\chi_g\rangle / \langle\chi_g|\chi_g\rangle \,]\, |\phi_p\rangle, \qquad \text{(III.10)}$$

$$i\hbar \frac{\partial}{\partial t} |\chi_g\rangle = [\, P^2/2M + V_{ia}(R) + \langle\phi_p|V_{ea}(r,R)|\phi_p\rangle / \langle\phi_p|\phi_p\rangle \,]\, |\chi_g\rangle, \qquad \text{(III.11)}$$

and

$$\frac{\partial}{\partial t}\eta_g = \langle\phi_p\chi_g|V_{ea}(r,R)|\chi_g\phi_p\rangle / \langle\chi_g|\chi_g\rangle \langle\phi_p|\phi_p\rangle \qquad \text{(III.12)}$$

The Hartree ground state energy is

$$E_g = \langle\phi_g|p^2/2m+V_{ei}(r)|\phi_g\rangle / \langle\phi_g|\phi_g\rangle + \langle\chi_g|P^2/2M+V_{ia}(R)|\chi_g\rangle / \langle\chi_g|\chi_g\rangle + \langle\phi_g\chi_g|V_{ea}(r,R)|\chi_g\phi_g\rangle / \langle\chi_g|\chi_g\rangle \langle\phi_p|\phi_p\rangle . \qquad \text{(III.13)}$$

In the Appendix B we show that the use of the Hartree approximation in the equations (III. 1-5) leads to several formulae for the cross section which are not equivalent to each other. The version presented above is the simplest and more accurate (i.e. for the present model it gives the closest results (but still poor) to the exact quantum calculations).

In Fig. 1 we compare the absorption cross section given by the TDH (Fig. 1a) with that obtained by exact quantum calculations (Fig. 1b). The spectrum consists of an electron excitation (at about 3.75 eV) and vibrational side bands due to the alkali-helium oscillations. The TDH calculation reproduces the intensities and the positions of the main peaks. It gives small negative absorption coefficients for a few frequencies, but the overall accuracy is satisfactory.

IV. The "Traditional" Quantum -Classical Method.

To calculate the overlap integral leading to the absorption cross section by the TQC method we use the wave function

$$\langle r,R \mid \Psi_p \rangle \approx \langle r \mid \phi_p \rangle \equiv \langle r \mid r \mid \phi_g \rangle \qquad \text{(IV.1)}$$

Compared to the TDH wave function (III.7-8) the equation (IV.1) neglects the wave function for the classical degrees of freedom and the Hartree phase η_g. With this assumption the overlap integral (III.9) becomes

$$C_{tqc}(t) = \exp(iE_g t/\hbar)\, \langle \phi_p(0) \mid U_{tqc}(t) \mid \phi_p(0) \rangle . \qquad \text{(IV.2)}$$

The subscript tqc indicates the use of the traditional quantum-classical method. The propagator $U_{tqc}(t)$ is the formal solution of the equation

$$ih\frac{\partial}{\partial t}|\phi_p\rangle = [\, p^2/2m + V_{ei}(r) + \langle V_{ea}(r,t)\rangle_R \,]\,|\phi_p\rangle; \qquad \text{(IV.3)}$$

In other words $U_{tqc}(t)|\phi_p(0)\rangle$ is solution of Eq. (IV. 3) with the initial condition $|\phi_p(0)\rangle$. The interaction between the quantum variable r and the classical one is given by

$$\langle V_{ea}(r,t)\rangle_R = \frac{1}{N}\sum_{n=1}^{N} V_{ea}(r,R_n(t)). \qquad \text{(IV.4)}$$

The position operator R in the interaction is replaced by its classical value at time t. To calculate this mean potential defined by Eq. (IV.4) we run a bundle of N trajectories whose initial conditions are sampled by a Monte Carlo procedure from a suitable distribution (see Section VI). $\langle V_{ea}(r,t)\rangle_R$ is the average of the electron - He interaction over these trajectories. The use of this average was suggested in Ref. 1d; it is consistent with the averaging that appears in the TDH equation (III.10). Most applications of the quantum-classical method use one trajectory.

The equation of motion for each of these trajectories is

$$M\, d^2R/dt^2 = -\partial\{\, V_{ia}(R) + \langle \phi_p(t)\,|V_{ea}(r,R)|\,\phi_p(t)\rangle \,\}/\partial R. \qquad \text{(IV.5)}$$

The second term on the right hand side of (IV.5) is the mean interaction between the quantum and the classical degree of freedom. Note a serious dynamic inconsistency of this scheme: the q - c interaction used in the time dependent Schrödinger equation is different from the q - c interaction used in the Newton's equation for the classical variables.

The time dependent Schrödinger equation (IV.3) and the classical equation (IV.5) are solved self-consistently. At time zero the Monte Carlo procedure generates the initial conditions for the classical trajectories. This gives a set of values $R_n(t=0)$, n=1,2,...N, which are used to calculate the mean potential (IV.4) which enters in Eq. (IV.3). Once this potential is known we propagate the wave function $|\phi_p\rangle$ for a time step τ and determine $\langle r|\phi_p,\tau\rangle$. This is then used to calculate the mean force in Eq. (IV.5) which is then solved to obtain $R_n(\tau)$ after a time step τ, for all n. If, for example, we propagate simultaneously one hundred trajectories, we solve simultaneously a hundred classical equations and the time dependent Schrödinger equation for $|\phi_p\rangle$.

This definition of the TQC procedure is not unique. For example we might have preserved the phase η_g appearing in (III.8) and solve

$$\frac{\partial}{\partial t}\eta_g = \frac{1}{N}\sum_{n=1}^{N} \langle\phi_p,t|V_{ea}(r,R_n(t))|\phi_p.t\rangle / \langle\phi_p,t|\phi_p,t\rangle \qquad \text{(IV.6)}$$

which is the quantum - classical version of Eq. (III.2). We experimented with such variations and found that they do not give better results.

In Fig.2 we compare the absorption spectrum calculated with the TQC

approximation to that given by the TDH calculation. The negative absorption rate at lower frequency (Fig.2a) is absurd: the intensity of a weak beam of light will grow exponentially as it penetrates a sample having this property. The positive peaks at higher frequency resemble the correct spectrum except for a downward shift of about 0.1 eV. One reason for its presence is the inability of the classical mechanics to reproduce the zero point energy of He after the excitation of the electron; the zero point energy of He when the electron is in the ground state is taken into account through the MC sampling.

Other versions of the TQC procedure (i.e. using one trajectory only, keeping in the quantum-classical theory the phase η_g introduced when the TDH approximation is made, using a slightly different formula for the absorption cross section (see Appendix B)) either do not improve the results or make them worse.

V. The need for a "classical wave function".

Previous[5] TDH calculations of the absorption spectrum of I_2 in an Ar matrix were in agreement with the experimental measurements. The results presented in Section III, and other calculations whose results are not reported, show that the TDH approximation gives a reasonable absorption cross section for the systems considered here. The absorption coefficient takes only small negative values. The spectrum does not deteriorate as the cut off time is increased form 100 fs to 600 fs.

Therefore, in the kind of examples considered here the large negative absorption coefficient in TQC does not come from the use of the TDH approximation, but from treating the dynamics of R classically. This involves two

kinds of approximations: the neglect of the wave function for R and the use of a swarm of trajectories to calculate the mean potential acting on the quantum degrees of freedom. The use of a mean interaction can lead to substantial errors when the wave function of the quantum degree of freedom splits into spatially disjoint pieces or becomes very delocalized[2]. This is not the case in the present examples: the wave function of the excited electron in the alkali atom is well localized. Moreover, if the mean potential were a source of error the TDH procedure, which uses a very similar mean potential, should also produce errors and it does not.

We are led therefore to suspect that the reason for the negative absorption coefficients in the TQC calculation is the absence of a wave function describing the behavior of the c-degrees of freedom; that is, the use of Eq. (IV.1) and its consequence (IV.2)). That approximation assumes implicitly that whatever is missed by removing the classical degrees of freedom from the total wave function, is made up through the action of the time dependent potential ($\langle V_{ea}(r,t)\rangle_R$ given by Eq. (IV.4)) appearing in the Hamiltonian for the quantum degrees of freedom (Eq. (IV.3)). This potential oscillates on a time scale set by the classical motion of the medium and this affects the electron's wave function. The random motion of the classical bath will dephase the quantum degrees of freedom and broaden the peaks in the spectrum. It will also cause energy exchange between the c and the q degrees of freedom, leading to sidebands in the spectrum. The potential may or may not do that, but unfortunately it also has the unfortunate effect of giving negative absorption coefficients and spurious side bands.

To demonstrate that the difficulties encountered by the TQC calculations are due to the suppression of the wave function for the c-degrees of freedom, we

have performed the numerical experiments described below. These "experiments" are conducted within the TDH approximation, which does not suppress the wave function for the c-degrees of freedom. This wave function contributes an additional term in the overlap integral used to calculate the absorption spectrum; one can say that the main approximation in the TQC method is to replace this additional term (i.e. $\langle\chi_g(0)\,|\,\chi_g(t)\rangle\ \exp(i\eta_g/\hbar)$ in Eq. (IV.2)) by one (compare (IV.2) to (III.9)).

The Fig.3a shows the spectrum obtained by using the correlation function

$$C_a(t) = \exp(iE_g t/\hbar)\,\langle\phi_p(0)\,|\,\phi_p(t)\rangle\,. \qquad (V.1)$$

instead of C(t) of Eq. (III.2). The correlation function formula for the absorption spectrum is the same as in the TQC procedure but the wave functions $|\phi_p(t)\rangle$, $|\phi_p(0)\rangle$ and the ground state energy E_g are calculated by solving the TDH equations (III.10-12), not by using the TQC dynamics.

The spectrum calculated without $\langle\chi_g(0)\,|\,\chi_g(t)\rangle$ is as bad as the one generated by the TQC procedure, even though we have use the TDH dynamics to perform the calculations. It has the same red shift of about 0.1eV, a large negative amplitude and an erroneous but small absorption peak at the red side of the fundamental peak. The close similarity between these two calculations confirms our statement that the poor results for the spectrum come from the c-wave function suppression.

Next we perform further experiments to try to understand how various parts of the c- wave function influence the calculated absorption spectrum. First

we perform a cross section calculation in which the overlap $\langle\chi_g(0)\,|\,\chi_g(t)\rangle$ is left out but the phase factor $\exp(i[\eta_g(t)-\eta_g(0)]/\hbar)$ is included. That is we use

$$C_b(t) = \exp(iE_g t/\hbar)\,\langle\phi_p(0)\,|\,\phi_p(t)\rangle\,\exp(i[\eta_g(t)-\eta_g(0)]/\hbar). \qquad (V.2)$$

instead of Eq.(III.9). The resulting spectrum is shown in Fig. 3b. There is a minor improvement but the negative absorption coefficient is painfully visible.

In Fig. 3c we show the spectrum obtained by using

$$C_c(t) = \exp(iE_g t/\hbar)\,\langle\phi_p(0)\,|\,\phi_p(t)\rangle\,\exp(i[\eta_g(t)-\eta_g(0)]/\hbar)\;|\;\langle\chi_g(0)\,|\,\chi_g(t)\rangle\,| \qquad (V.3)$$

which includes the absolute value of $\langle\chi_g(0)\,|\,\chi_g(t)\rangle$.

Fig. 4d shows the one obtained by using

$$C_d(t)=\exp(iE_g t/\hbar)\langle\phi_p(0)\,|\,\phi_p(t)\rangle\exp(i[\eta_g(t)-\eta_g(0)]/\hbar)\langle\chi_g(0)\,|\,\chi_g(t)\rangle/|\,\langle\chi_g(0)\,|\,\chi_g(t)\rangle| \qquad (V.4)$$

which contains only the phase of $\langle\chi_g(0)\,|\,\chi_g(t)\rangle$. The results show that $\langle\chi_g(0)\,|\,\chi_g(t)\rangle$ makes its most important contribution to the cross section through its absolute value.

The main conclusion of this section is that to obtain good spectra by a QC method *we need a reasonable approximation to* $\langle\chi_g(0)\,|\,\chi_g(t)\rangle$, *or at least to* $|\,\langle\chi_g(0)\,|\,\chi_g(t)\rangle|$. The replacement of the overlap of the c-wave functions with one - which is made in the TQC method - is not tenable. The physical reason for this is

discussed in Section VII, where we also suggest better and more efficient approximations.

VI. The classical wave function

To obtain a wave function for the c- degrees of freedom from classical trajectories we write the c-wave function $\chi(R,t)$ as

$$\chi(R,t) = A(R,t) \exp[\, i\, S(R,t) / \hbar]. \qquad \text{(VI.1)}$$

where A and S are real functions. Inserting this form into the time dependent Schrödinger equation leads to[13]

$$\frac{\partial}{\partial t} S + (\nabla S)^2 / 2M + V_{ei}(R) + \langle \phi_p(t) \,|V_{ea}(r,R)|\, \phi_p(t) \rangle - (\hbar^2 / 2MA)\nabla^2 A = 0 \qquad \text{(VI.2)}$$

and

$$\frac{\partial}{\partial t} A^2 + \nabla (A^2 \nabla S / M) = 0. \qquad \text{(VI.3)}$$

One can show[13] that

$$A(R,t)^2 = \int dR'\, \chi(R',t)^* \delta(R-R') \chi(R',t) \qquad \text{(VI.4)}$$

is the particle density at the point R and

$$A(R,t)^2\nabla S(R,t)/M=\int dR'\chi(R',t)^*\{(\hat{P}/M)\delta(R-R')+\{\delta(R-R')(\hat{P}/M)\}\chi(R',t) \qquad \text{(VI.5)}$$

is the mean particle flux through the unit area located at R. Thus both S and A are related to the expectation values of operators (i.e. the density and the flux operators) having a well defined classical meaning. As we have already pointed out in the introduction we expect methods based on classical dynamics to work better when applied to quantities that have a physical meaning in the classical limit.

To calculate classically A(R,t) and S(R,t), hence the wave function χ (R,t) = A(R,t) exp[i S(R,t) / $\hbar$] which has been discarded by the TQC, we use the method described below. This is based on the well known observation that when the "quantum force" $(\hbar^2/2MA)\nabla^2 A$ is negligible the Eq. (VI.2) resembles the Hamilton Jacobi equation[14] of classical mechanics. We construct a solution of this equation by running a swarm of classical trajectories with initial conditions generated by a Monte Carlo procedure designed to mimic the information provided by the initial wave function for the degree of freedom R. That procedure is described later in this section. To construct solutions of the Eq. (VI.1) and (VI.2) (with the quantum term absent) we discretize the variable R and denote by R_1, .. R_i ,... the discrete points. The value of the function A(R,t) at R_i is defined as the square root of the density of trajectories present in the bin in which R_i is located. The value of S(R,t) at R_i is given by

$$S(R_i,t) =(1/N)\sum_{\alpha}^{N} s_\alpha(t)\chi_i \qquad \text{(VI.6)}$$

where

$$s_\alpha(t) = \int_0^t dt\{P_\alpha(t)R_\alpha(t) - H[R_\alpha(t), P_\alpha(t)]\} \qquad \text{(VI.7)}$$

is the classical action for the trajectory α and χ_i restricts the sum in Eq. (VI.6) to those trajectories that are, at time t, in the bin containing R_i.

This procedure is justified as follows. If we define

$$P(R_i,t)^2 = \sum_{\alpha_i(t)} p_\alpha(t)^2 \qquad \text{(VI.7)}$$

then the quantities $S(R_i,t)$ and $P(R_i,t)$ satisfy Eq.(VI.2) without the quantum term. This is true because the quantities s_α and p_α satisfy the Hamilton Jacobi equation[14]. Note that the definition

$$P(R_i,t)^2 = \{ \sum_{\alpha_i(t)} p_\alpha(t) \}^2$$

would not lead to a solution of (VI.2).

To complete the procedure we must provide a sampling rule. We use the probability $|\chi_E(R,0)|^2$, provided by the initial wave function for the variables to be treated classically, to generate (by Metropolis sampling) an initial value for R, which we denote R_0. Then we use the equation

$$P_0 = \pm \{ 2M [E - E_q(R_0) - V_{ia}(R_0)] \}^{1/2}. \qquad \text{(VI.9)}$$

to calculate an initial momentum P_0. Here E is the total energy of the system and

$E_q(R_o)$ is the energy of the quantum subsystem when $R=R_0$. If P_0 is imaginary we reject R_0 and try again. If it is real we accept $\{P_0, R_0\}$ and $\{-P_0, R_0\}$ as initial conditions. We repeat the procedure until several hundreds of initial conditions are generated. These initial conditions are then used to generate the swarm of trajectories. The swarm and the wave function for the quantum degree of freedom are propagated self-consistently by solving the simultaneously the equations (IV.3-5).

The sampling rule is not unique and many other procedures are available. The one used here attempts to put into the classical initial conditions the physical information contained in the initial wave function: the total energy and the position distribution for the degree of freedom to be treated classically.

The replacement of $\chi(R,t)$ in the Hartree correlation function of Eq.(III.11) by the "classical wave function" $A(R;t)\exp(iS(R;t)/\hbar$ gives

$$C_{qc}(t) = \exp(iE_g t/\hbar)\,\langle\phi_p(0)\,|\,\phi_p(t)\rangle\,\langle\chi(R,0)\,|\,\chi(R,t)\rangle_c\,\exp(i\lambda(t)/\hbar). \qquad \text{(VI.14)}$$

The subscript qc denotes a QC calculation. The "classical" overlap term is

$$\langle\chi(R,0)\,|\,\chi(R,t)\rangle_c = \int dR\, A(R,0)\exp(-iS(R,0)/\hbar)\,A(R,t)\exp(iS(R,t)/\hbar) \qquad \text{(VI.15)}$$

and the ground state energy is

$$E_g = \langle \phi_g | \{ p^2/2m + V_{ei}(r) + \langle V_{ea}(r) \rangle_R \} | \phi_g \rangle / \langle \phi_g | \phi_g \rangle + \frac{1}{N} \sum_{n=1}^{N} [P_n{}^2/2M + V_{ia}(R_n)]. \qquad \text{(VI.16)}$$

Since the trajectories are calculated after the Monte Carlo sampling generates the initial positions and momenta, the sampling weight does not appear in the sum (i.e. the sum is calculated by the Monte Carlo procedure). The Hartree phase term

$$\lambda(t) = \eta(t) - \eta(0) \qquad \text{(VI.17)}$$

in (VI.14) is

$$\lambda(t) = \int_0^t dt' \langle \phi_p(t') | \frac{1}{N} \sum_{n=1}^{N} V_{ea}(r, R_n(t')) | \phi_p(t') \rangle / \langle \phi_p | \phi_p \rangle. \qquad \text{(VI.18)}$$

This sum is also calculated by the Monte Carlo procedure and the Monte Carlo weight does not appear in the sum.

We note other procedures that use similar algorithms to generate wave functions or other time dependent quantum amplitudes. Recently Heller[15] presented an interesting implementation of the semiclassical formula[16] for the time dependent propagator. A different method, proposed by Olson and Micha[17a], has been used in the time dependent theory of photo-dissociation[17b].

In Fig. 4, we compare the spectrum obtained by using the QC correlation function of Eq.(VI.14) with the TDH spectrum (which is practically exact). The

large negative cross section (that appears in the TQC calculation) has disappeared. The band head position is still shifted by about 0.1eV; this happens, in part, because classical dynamics does not give the R degree of freedom a zero point energy in the excited state of the electron.

To better understand how various elements of the classical wave function affect the spectrum we have performed calculations similar to those described in Fig. 3, except that we have replaced the TDH procedure with the method described in section. The results are very similar to those presented in Fig. 4 and are not given here. The most important contribution to the spectrum is made by the quantity

$$|\langle\chi(R,0)|\chi(R,t)\rangle_e| = \left\{\int dR\, A(R,0)\, A(R,t)\cos(S(R,t)/\hbar)\right\}^2 + \left\{\int dR\, A(R,0)\, A(R,t)\sin(S(R,t)/\hbar)\right\}^2$$

The phase S(R,t) of the classical wave function is important, but the phase of $\langle\chi(R,0)|\chi(R,t)\rangle_e$ is not.

Calculations on a system mimicking the HIAr system, in which the hydrogen atom is treated quantum mechanically and Ar is treated classically lead to similar results. This suggests that the conclusions of our analysis are not system dependent.

VII. Summary and discussion.

The present calculations have shown that the TQC method can give physically absurd results (e.g negative absorption coefficients) when used to

compute absorption cross sections, and perhaps other quantities that do not have a simple classical interpretation. Several numerical experiments have been performed to determine the source of error. They established that (a) the TDH calculations give good results for the system of interest here (confirming the conclusions of Messina and Coalson[12]). (b) If we perform TDH calculations but remove - from the equation for the absorption cross section - the overlap integrals corresponding to the c-degrees of freedom we obtain again negative absorption coefficients. This indicates that the source of the error is not the use of classical dynamics to find the mean time dependent interaction between the electron and the classical degrees of freedom, but the absence of a wave function for the classical degrees of freedom. The TQC method approximates (in the formula giving the cross section) the overlap integrals for the c-degrees of freedom by one. Our "experiments" have shown that this is a particularly unfortunate choice. (c) One can use classical trajectories to calculate the overlap integrals in the formula for the absorption coefficient, to obtain satisfactory results.

In this section we examine in more detail why TQC fails. This analysis also leads us to suggest a computational method that is likely to give good results for the spectrum of an impurity in a condensed medium. For concreteness we consider a one electron atom imbedded in a medium. The analysis and its conclusions are generally applicable.

Within the TDH approximation the absorption cross section is determined (see (III.1-4)) by the overlap integral

$$C(t) = \langle \zeta_p , t | \zeta_p , 0 \rangle \prod_{i=1}^{N} \langle \phi_i, t | \phi_i, 0 \rangle \qquad \text{(VII.1)}$$

Here $|\zeta_p, 0\rangle = x\,|\zeta_g, 0\rangle$ is the promoted state of the electron. The electronic contribution $\langle\zeta_p, t|\zeta_p, 0\rangle$ gives the positions of the atomic absorption lines; the overlaps $\langle\phi_i, t|\phi_i, 0\rangle$ give these lines a width and generate vibrational side bands (if any). We concentrate now on understanding the properties of the product of nuclear overlap integrals, by using methodology developped by Heller[3].

In the absorption cross section formula the atoms of the medium are in their ground state at time zero. Their potential energy is given by

$$V_g(R) = \int dr\, \zeta_g(r, R, t=0)\, V(r, R)\, \zeta_g(r, R, t=0). \qquad \text{(VII.2)}$$

Here R is a symbol for all the atomic positions, $\zeta_g(r, R, t=0)$ is the ground state electron wave function and V is the electron - medium interaction energy. At time zero the medium's atoms are located around the positions R_g which minimize $V_g(R)$.

When we start the absorption cross section calculation the Heller formula requires us to place the electron in the promoted state $\zeta_p(r,R,t=0) = -x\,\zeta_g(r,R,t=0)$. The potential energy felt by the atoms of the medium is now

$$V_p(R) = \int dr\, \zeta_p(r, R, t=0)\, V(r, R)\, \zeta_p(r, R, t=0). \qquad \text{(VII.3)}$$

The equilibrium positions R_p appropriate to the "promoted electron" state

minimize V_p (R) and differ from R_g. As a result at a time immediately after zero, the force

$$F = - \frac{\partial V_p(R_g)}{\partial R_g} \qquad \text{(VII.4)}$$

on the medium's atoms is finite and pushes them away from R_g, towards R_p. As a result, all the overlap integrals in Eq. VII.1 will become smaller in a very short time. To this Hellerian[3] analysis we add an important observation made by Nitzan[18] in connection with the rate of radiationless transitions: If a sufficiently large number of the medium's atoms are affected by the "promotion" of the electron, their overlap integrals $\langle \phi_i,t \mid \phi_i,0 \rangle$ will *all* start decreasing and their product in Eq. (VII. 1) will decrease *very rapidly*. This has an extremely important consequence: larger the number of atoms coupled to the electron, shorter the time needed for the calculation of the absorption cross section!

In what follows we show that this time can be so short that the atoms of the medium do not have time to sample the potential energy surface; as a result the latter can be described by a local harmonic approximation. This makes it possible to apply Heller's Gaussian wave packet (GWP) method[3b] to describe the quantum dynamics of the atoms in the medium with high accuracy. The outcome is that a method using the TDH approximation and treating the medium's atom by a Gaussian wave packet method and the electron exactly will give very good results for the absorption cross section for large systems. Moreover, larger the system, better the results!

Let us assume that the time in which the *product* of the overlaps decays

is so short that, for the duration of the decay, we can use a harmonic approximation for the forces acting on the medium's atoms. This allows us to use the short time analysis employed by Heller, Sundberg and Tannor[3d] in their discussion of Raman spectra, to determine the decay time and test whether it is as short as assumed. For simplicity we treat the medium's atoms as independent harmonic oscillators (i.e. we use an Einstein model). One can refine the argument by using normal modes etc., but its essence is not altered by our simplification. The initial wave function for one of these oscillators is

$$\phi(R,t=0) = (m\omega_g/\pi\hbar)^{1/4} \exp[-m\omega_g R^2/2\hbar] \qquad \text{(VII.5)}$$

Here ω_g is the local harmonic frequency obtained from the force constant $\partial^2 V_g/\partial R_g^2$. We use a coordinate system centered at R_g. When the electron is promoted this wave function moves under the influence of the potential V_p. For a short time this motion can be treated by Heller's frozen Gaussian method[3b]. This means that at the time t the wave function has the form

$$\phi(R,t) \sim \exp[-m\omega_g (R-R(t))^2/2\hbar] \exp[iP(t)(R-R(t))] \qquad \text{(VII.6)}$$

Since we want to calculate the decay of the overlap integral we ignore here the phase factors and the normalization constant. A detailed analysis and an algorithm based on these observations will be presented elsewhere[19]. The overlap integral is

$$\int dR\phi(R,t)^*\phi(R,0) \sim \exp[-P(t)^2/2\hbar\omega_g m] \sim \exp[-(F\,t)^2/(2\hbar\omega_g m)] \qquad \text{(VII.7)}$$

We have used the fact that for a very short time the classical momentum $P(t) = F\,t$, where F is the force given by (VII.8). We see that the earliest evolution of the overlap integral for one atom of the medium is a Gaussian decay with time. The time scale of this decay is

$$\tau = (2\hbar\omega_g m)^{1/2}/F \qquad \text{(VII.8)}$$

We can estimate the magnitude of this time as follows. In the local harmonic approximation $F = m\omega_p(\delta R_e)^2$ where ω_p is the oscillator frequency when the electron is in the promoted state and δR_e is the difference $R_p - R_g$ between the equilibrium position R_p of the atom when the electron is in the promoted state and the equilibrium position R_g when the electron is in the ground state. Furthermore, $2\hbar/(m\omega_g) = \langle\delta R_g\rangle^2$ where $\langle\delta R_g\rangle^2$ is the mean square displacement of the oscillator when the electron is in the ground state. Using these equations in (VII.11) leads to the estimate

$$\omega_p\,\tau = \{(\omega_g/\omega_p)\}^{1/2}(\delta R_p/\delta R_e)$$

If we make the reasonable assumptions that $\omega_g \sim \omega_p$ and $\delta R_p < \delta R_e$ then τ is less than ω_p^{-1}. If we take $\omega_p = 200\ cm^{-1}$ and assume $\tau \approx \omega_p^{-1}$, the overlap integral is equal to 0.014 in 75 femtoseconds. If the promotion of the electrons disturbs n = 10

atoms, the spectrum depends on the product of the ten overlap integrals and the decay time of the product is roughly τ/n. Numerical calculations using Eq. (VII.7) and the estimates explained above show that the product of ten Gaussians is equal to 0.003 in a 7.5 femtoseconds. For n=12 tbe product is equal to 0.0001 in 3 femtoseconds. Within this short time the displacement of the heavy medium atoms is very small and this justifies the local harmonic approximation and makes the argument self-consistent.

The main observation here is that if the electron (or the impurity degrees of freedom generating the spectrum) is coupled to *many* nearby atoms, the time needed to calculate the spectrum is extremely short. This is true regardless of how slow (i.e. heavy) these atoms are, which is somewhat counter-intuitive. This allows the use of simpler methods which treat accurately short time quantum dynamics: the Gaussian wave packet method[3b], the expansion proposed by DePristo *et al*[20], analytic continuation methods, quantum Monte Carlo methods or the Magnus (cumulant) approximation. We are currently pursuing some of these[19].

The fast decay of the product of overlap integrals also explains the failure of the TQC method, which replaces this product with one. Paradoxically, a method that was designed to help when the medium has many degrees of freedom becomes less and less useful as the number of the mediums atoms that affect the electron is increased. The only application left for the method, in the field of absorption spectroscopy, is to the study of inhomogeneous broadening by static disorder[21].

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Appendix A: Computational details

A.1 The initial state

The initial ground state wave functions for both the exact quantum calculation and the Hartree approximation is calculated by acting with the exp[–αH] on an arbitrary wave function with the appropriate symmetry. As the real number α becomes larger the result converges towards the ground state of the Hamiltonian H. For propagation we use a method proposed by Fleck, Morris and Feit[22].. The numerical procedure has been described by Hellsing, Nitzan and Metiu[23] . Others[24] have used a very similar procedure in a different context.

A.2 The time evolution of the promoted state

The quantum time propagation is performed with the algorithm of Fleck, Morris and Feit[21] and the classical equation of motion is solved with the Verlet[25] algorithm.

For the fully quantum calculations we have used a time step of 0.01 fs and a spatial grid having 48X96 points with a spacing of 0.6 Å in the r-coordinate and 0.067Å in the R-coordinate. The results were checked for convergence by making the spatial and temporal steps smaller until the result did not change. Increasing the number of points in the spatial grid shifted the ground state energy of the electron by less than 1%. We typically propagate the system in time for 100-300 fs. This space-time grid results in better than 0.1% conservation of energy over a 100 fs time span for the quantum propagator.

In the Verlet algorithm[25] the time step of 0.01 fs was used. The total

energy was conserved to better than 0.1% over 300 fs. The absorption cross section converges when the number of trajectories is between 200 and 600.

Appendix B: Various formulae for the cross section.

Often the same approximation applied to several equivalent formulae leads to procedures having different accuracy computer power requirements. As shown below this happens when the TQC approximation is applied to the formula giving the absorption cross section. We can write the correlation function used in Chapter III as

$$C(t)= \langle\Psi_g | r \exp(iHt/\hbar)\, r \exp(-iHt/\hbar) | \Psi_g\rangle^* = \langle\Psi_p,t |\ r\ | \Psi_g,t\rangle^* . \qquad (B.1)$$

where $|\Psi_g\rangle$ is the ground state at time zero, $|\Psi_g,t\rangle$ is the ground state at time t, and $|\Psi_p,t\rangle$ is the promoted state (see Eqs. (III.3-4) for definition) at time t. If exact quantum calculations are performed Eq. (B.1) is equivalent to Eqs. (III.2-4). However if we make the same dynamical approximation in these equivalent equations the results are different.

The Hartree approximation in Eq.(B.1) leads to

$$C(t) = \langle\phi_g,t | r | \phi_p,t\rangle\langle\chi_g,t | \chi_p,t\rangle\exp(i[\eta_p(t)-\eta_g(t)]/\hbar). \qquad (B.2)$$

To calculate a spectrum by this formula we must propagate (by TDH or by a TQC method) both the ground and the promoted state.

We have found that, whether we use a TDH or a TQC method of propagation this, this prescription works less well than the approach outlined in

Section III.

A similar form is obtained if we derive the Heller formula directly from the time dependent perturbation theory. The state created by the laser is proportional to

$$|\Psi,t\rangle \sim \int_0^t dt_1 U(t-t_1)F(t_1)U(t_1)|\Psi_g\rangle$$

where $|\Psi_g\rangle$ is the ground state of the system,

$$F(t) = -\mathbf{er}\cdot\mathbf{E}(t),$$

and U(t) propagates the system's wave function (electromagnetic field not included) from zero to t. The rate of growth of the population created by the laser, which is essentially the absorption cross section is

$$d\langle\Psi,t|\Psi,t\rangle/dt \sim \mathrm{Re}\int_0^t dt_1 \langle\Psi_g|U(-t)F(t)^*U(t-t_1)F(t_1)U(t_1)|\Psi_g\rangle$$

This equation can be used whether the excitation is caused by a short pulse or by a cw source. In the latter case the propagation time t determines the spectral resolution. Applying the TDH or the TQC procedure to this equation, which is equivalent to Heller formula, leads to yet another prescription. If the TQC propagation scheme is used this procedure also leads to negative absorption coefficients.

FIGURE CAPTIONS

Fig. 1 A comparison of the absorption spectra obtained from Eq. III.5 with τ = 100fs, by using two methods for calculating C(t): (a) The correlation function C(t), given by Eq. III.9 was calculated with the time-dependent Hartree (TDH) approximation; (b) C(t), given by Eq. (III.2) was calculated quantum mechanically (i.e. no approximations). The spectrum, in arbitrary units, is plotted versus photon energy in eV.

Fig. 2 A comparison of the absorption spectra obtained from Eq. III.5 with τ = 100 fs by using two different methods for computing C(t): (a) the "traditional quantum-classical (TQC) approximation with C(t) given by Eq. (IV.2) ; (b) the time dependent Hartree (TDH) with C(t) given by Eq. (III.9). The absorption spectrum in arbitrary units is plotted versus photon energy in eV.

Fig. 3 The absorption spectra (in arbitrary units) versus energy (in eV) by suppressing various components of the TDH correlation function (Eq. III.9):
(a) spectrum calculated by using Eq. (V.1) in which C(t) contains only the overlap of the electron promoted wave function; (b) same as (a) but the contribution of the Hartree phase is no longer removed from C(t) (we use Eq. (V.2)); (c) same as (b) but the amplitude of the nuclear wave function overlap is no longer suppressed from C(t) (we use Eq. (V.3)); (d) the spectrum without suppressing any component of the overlap. This is the correct TDH spectrum which is close to the correct fully quantal calculation.

Fig. 4 A comparison of the absorption spectra obtained by using two different methods for the calculation of C(t): (a) the classical wave function (QC) approximation is used for the nuclear dynamics with C(t) given by Eq. (VI.14); (b) time dependent Hartree (TDH) is used for the dynamics and C(t) is given by Eq. (III.9). The absorption coefficient is in arbitrary units and the photon energy in eV.

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